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RESEARCH MEMORANDUM

IGNITION DELAYS OF SOME NONAROMATIC FUELS WITH LOW-FREEZING RED FUMING NITRIC ACID IN TEMPERATURE RANGE -40° to -105° F

By Riley O. Miller

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

IGNITION DELAYS OF SOME NONAROMATIC FUELS WITH LOW-FREEZING RED FUMING NITRIC ACID IN TEMPERATURE RANGE -40° TO -105° F

By Riley O. Miller

SUMMARY

With low-freezing red fuming nitric acid in a modified open-cup apparatus, ignition delays were determined in the temperature range -40° to -105° F for allylamine, diallylamine, mixed alkyl thiophosphites, ethylenimine, blends of each of these fuels with triethylamine, and blends of ethylenimine with n-heptane. The data indicate that allylamine, mixed alkyl thiophosphites, and ethylenimine can be blended with as much as 70 percent triethylamine and still ignite with average delays less than 30 milliseconds at -40° F, and approximately 40 milliseconds at -76° F (-60° C). At -105° F (with supercooled acid), blends of 50 percent allylamine in triethylamine or 50 percent ethylenimine in triethylamine gave average delays of 50 and 33 milliseconds, respectively. Ethylenimine diluted 50 percent with n-heptane ignited with average delays of 60 and 104 milliseconds at -40 and -105° F, respectively.

INTRODUCTION

An important consideration in the starting of a rocket engine by injecting a small amount of fuel spontaneously ignitible with the oxidant is the ignition delay (time from fluid contact to flame). Ignition delays of the order of 50 milliseconds are low enough for rapid engine starting and lessen the danger of an accumulation of unreacted materials in the combustion chamber. It thus becomes of interest to determine the ignition delay of fuels and how the delay is affected by the low temperatures that may be encountered in practical operation.

The suitability of various nitric acid - fuel combinations for starting acid-gasoline engines is being investigated at the NACA Lewis laboratory (references 1 to 4). It has been found (references 3 and 4) that red fuming nitric acids containing 3 to 4 percent water and

16 to 19 percent nitrogen tetroxide were desirable because: (1) they have low freezing points (-87° to -88° F), (2) they can ignite a number of fuels at temperatures of -76° F and lower, and (3) they have lower equilibrium decomposition pressures than white fuming nitric acids (reference 5), an important consideration if the acid in storage reaches high temperatures (100° to 160° F). Fuels found to have short ignition delays with low-freezing red fuming nitric acid are blends of aromatic amines with triethylamine (references 3 and 4).

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Results of a program designed to enlarge the choice of fuels giving short ignition delays with low-freezing red fuming nitric acid at very low temperature are described herein. Ignition-delay data were obtained for the following nonaromatic fuels: allylamine and diallylamine (reference 6), mixed alkyl thiophosphites (reference 7), ethylenimine (reference 8), and 2-ethylethylenimine. The ignition delays at -40°, -76°, and -105° F of several blends of these fuels with triethylamine were also studied because triethylamine (first tried in German rocket fuels) has desirable physical properties, leaves little adhesive residue in a rocket chamber after shutdown, and was found (reference 3) to decrease the ignition delays of certain fuels. In the case of ethylenimine, n-heptane was also studied as a blending agent. The ignition-delay data presented herein were obtained by use of a modified open-cup apparatus (references 2 and 3).

APPARATUS

The ignition-delay data were obtained by means of a modified open-cup apparatus described in references 2 and 3, in which an ampule of fuel is broken in a cooled test tube containing the acid. The ignition delay, as determined, is the interval between the instant the ampule starts to break and the start of continuous flame, which is determined from cathode ray oscillograms showing light emission as a function of time. (High-speed photographs (reference 2) indicate that the ampule breaks in less than 2 milliseconds.) Oscillograms are also made of the sound of the reaction. In addition, the experiments are monitored by an electronic timer which is stopped by a flash of light. Unless otherwise indicated, the data herein are values determined directly from the light emission - time records.

MATERIALS

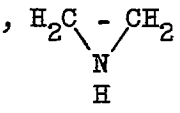
Fuels. - The following fuels were investigated:

Allylamine, $CH_2=CH-CH_2-NH_2$

[redacted]

Diallylamine, $(CH_2=CH-CH_2)_2NH$

Mixed alkyl thiophosphites, $(R-S)_3 P$

Ethylenimine, 

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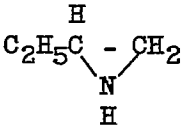
2-Ethylethylenimine, 

Triethylamine, $(C_2H_5)_3N$

The mixed alkyl thiophosphites fuel was supplied by the U.S. Air Force. The other fuels were purified compounds purchased from commercial sources.

Acid. - The low-freezing red fuming nitric acid was prepared by adding a calculated amount of distilled water to cold c.p.-grade red fuming nitric acid to obtain an acid containing approximately 3 percent water and 19 percent nitrogen tetroxide. The stock acid was analyzed by the method prescribed in U.S. Air Force acid specifications.

RESULTS AND DISCUSSION

Ignition delays of various fuels and fuel blends with low-freezing nitric acid at -40°, -76°, and -105° F are summarized in tables I to IV. The significant trends are further illustrated by plots of average ignition delays at the several temperatures as functions of fuel composition (figs. 1 to 4).

Allylamine, Diallylamine, and Their Triethylamine Blends

Comparison of allylamine and diallylamine at -40° F. - As shown by figure 1 and table I, unblended diallylamine gave a shorter delay than unblended allylamine (47 as compared with 91 milliseconds). The addition of triethylamine, however, decreased the delays of allylamine; a low range of 21 to 39 milliseconds (average) occurred at 50 to 85 percent triethylamine. Adding triethylamine to diallylamine increased the ignition delay; no minimum was observed for the blends investigated.

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Effect of low temperature on ignition of allylamine and its blends. - The ignition delays of allylamine with triethylamine at -40°, -76°, and -105° F are compared in figure 2. At each temperature the ignition delays were found to pass a minimum and increase sharply as the concentration of triethylamine was increased. As the temperature decreased the sharp increase in ignition delay occurred at lower triethylamine concentrations. Of the blends investigated, 50 percent allylamine gave the shortest average delays at -40°, -76°, and -105° F (21, 27, and 50 milliseconds, respectively).

Ignition of amine fuels. - The hypothesis has been proposed (reference 9) that ignition of amine fuels may depend in part upon preliminary neutralization reactions, between amino groups and the acid, which evolve heat and bring the fuel-acid mixture to temperatures at which other reactions leading to oxidation can take place. The data for the allylamine and diallylamine blends with triethylamine offer some evidence to support this hypothesis.

The kinetics of hypergolic ignition processes are not known, but a qualitative evaluation of the contributions of two possible reactions may assist in rationalizing the ignition behavior of the aliphatic amine blends used in this investigation. Neutralization seems likely to be the first reaction to occur between the amine and the acid. In the fuel, the second reaction may be bond fission, which would presumably take place at the lowest-energy bonds.

The assumption that neutralization and bond fission are the initiating reactions is in accordance with the ignition behavior of ammonia, hydrazine, and amines. Ammonia (NH_3), a nonhypergolic fuel is an example of a fuel with strong neutralizing power but no low-energy bonds. Hydrazine (H_2N-NH_2), a fuel that ignites readily with nitric acid, has both high neutralizing power (amino groups) and low-energy bonds (N-N). Aliphatic amines (RNH_2, R_2NH, R_3N), the self-igniting fuels of concern in this discussion, contain not only amino groups but also low-energy C-N bonds.

If the foregoing assumption is valid, ignition of aliphatic amines depends upon (1) concentration of amino groups and (2) concentration of C-N bonds. In the case of allylamine-triethylamine blends, concentration of one is gained at the expense of the other; allylamine has the larger concentration of amino groups, but triethylamine has the larger concentration of C-N bonds.

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Inasmuch as neutralization of amino groups results in a temperature effect (both upon neutralization itself and on subsequent reactions), the concentration of amino groups would be expected to have a higher order effect on the over-all reaction rate than concentration of C-N bonds; this is in agreement with the trends shown in figure 2. On the left side of figure 2 (high allylamine concentration), according to the hypothesis, more than enough amino groups are available in the fuel to bring the mixture to temperature at which bond rupture occurs rapidly and the concentration of C-N bonds is the limiting factor, but on the right side (high triethylamine concentration), the expected higher order effect of diminishing amino group concentration in decreasing reaction rate becomes apparent in the longer ignition delays.

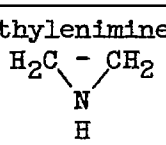
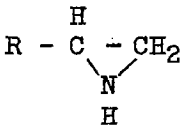
Ignition of Mixed Alkyl Thiophosphites and its Triethylamine Blends

The average ignition delays of mixed alkyl thiophosphites and its blends with triethylamine (table II) were very similar at -40° and -76° F, as shown by figure 3. The ignition delays were short for the unblended fuel (9 millisec average); for mixtures containing 50 to 70 percent triethylamine, the average delays at both temperatures were no greater than 41 milliseconds. At -105° F, however, the ignitibility of the fuel and its blends was severely impaired; the unblended fuel showed delays greater than 1 second, and blends of 50 percent or more triethylamine did not ignite. At all temperatures, the unblended fuel ignited the most readily, and the ignition delays increased with increased triethylamine content.

Ignition of Ethylenimine and its Triethylamine and n-Heptane Blends

Comparison of ethylenimine and 2-alkylethylenimines. - Ignition delays of ethylenimine fuels and blends are compiled in table III. Ethylenimine at -40° F gives delays approximately 1/3 as long as 2-ethylethylenimine with the low-freezing red fuming nitric acid; a similar tendency was found with 2-methylethylenimine and 90 percent white fuming nitric acid (reference 8) as shown by the following table:

[redacted]

Fuel	Average ignition delay at -40° F, milliseconds	
	Low-freezing red fuming nitric acid	90 Percent white fuming nitric acid (reference 8)
Ethylenimine 	12	≈30
2-Alkylethylenimine 	(R = ethyl) 39	(R = methyl) ≈120

Substitution of a 2-alkyl group appreciably decreases the self-igniting tendency of ethylenimine.

Blends of ethylenimine with triethylamine and n-heptane. - The effects of adding triethylamine or n-heptane to ethylenimine are shown by figure 4. Unblended ethylenimine exploded violently at both -40° and -105° F, with an average delay of 12 milliseconds at -40° F. No explosions were encountered with the blends. The ignition delays increased as the concentration of the blending agents was increased. Blends of triethylamine at both temperatures gave consistently shorter average ignition delays than blends of n-heptane; nevertheless, the average delays of 60 and 104 milliseconds (at -40° and -105° F, respectively) are remarkably short for a fuel diluted to 50 percent by a hydrocarbon.

Comparison of Triethylamine Blends

A comparison of allylamine, mixed alkyl thiophosphites, ethylenimine, and their respective triethylamine blends is shown in table IV. These data show that at -40° F all three fuels can be diluted with as much as 70 percent triethylamine and still ignite with low-freezing nitric acid with average delays less than 30 milliseconds. At -76° F these blends of allylamine and mixed alkyl thiophosphites each gave average delays of only 41 milliseconds; the behavior of ethylenimine would probably be comparable. The 50-percent blends of allylamine and ethylenimine in triethylamine gave the most satisfactory ignition at -105° F with average delays of 50 and 33 milliseconds, respectively. These delays are considerably shorter than those obtained at -105° F with blends of aromatic amines in triethylamine (reference 3).

[redacted]

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Explosions

Both ethylenimine and mixed alkyl thiophosphites, when undiluted (tables II and III) showed tendencies to explode with the acid. Experience with other fuels (references 3 and 4), however, shows that explosions in the modified open-cup apparatus may not be indicative of damaging explosions in a rocket engine.

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Residue Forming Properties

In the modified open-cup apparatus, the fuels discussed herein left less adhesive residue after ignition than did either aromatic amine or furan fuels. Unpublished data from rocket experiments substantiate this observation for 50 percent alkylamine plus 50 percent triethylamine and for mixed alkyl thiophosphites.

Appraisal

On the basis of short ignition delays with low-freezing red fuming nitric acid, the data presented herein indicate that, of the self-igniting fuels so far studied at this laboratory (references 2 to 4), 50-percent blends of allylamine or ethylenimine in triethylamine show the most promise for use at extremely low temperature (-105° F). Of these two fuels, the allylamine blend is probably the more promising on the basis of potential availability and ease of handling. Studies of the feasibility of expanded production of aliphatic amines by the petroleum industry may be warranted. At temperatures as low as -76° F, mixed alkyl thiophosphites appear to be a satisfactory self-igniting fuel. A final appraisal of these and other fuels, however, must await rocket engine experiments.

SUMMARY OF RESULTS

By use of a modified open-cup apparatus, ignition delays of several nonaromatic fuels and fuel blends were determined at -40°, -76°, and -105° F with low-freezing red fuming nitric acid containing approximately 3 percent water and 19 percent nitrogen tetroxide (acid supercooled at -105°F). The following trends were observed:

1. Blends of allylamine with triethylamine showed lower average ignition delays than the parent fuels. For the blends investigated, the minimum average delay and the composition ranges at three low temperatures were as follows:

Temperature (°F)	Triethylamine in blend (percent by volume)	Average ignition delay (millisec)
-40	50 to 85	21 to 39
-76	50 to 70	27 to 41
-105	50	50

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At -40° F none of the diallylamine - triethylamine blends investigated showed minimum average ignition delays. The average delays at -40° F for unblended allylamine and diallylamine were 91 and 47 milliseconds, respectively.

2. Mixed alkyl thiophosphites at -40° and -76° F gave average delays of 9 milliseconds, and the delays increased with increased triethylamine content but were less than 41 milliseconds for a blend containing 70 percent triethylamine. At -105° F, however, mixed alkyl thiophosphites showed an average delay greater than 1 second and the blends containing 50 percent or more triethylamine did not ignite.

3. Ignition delays of ethylenimine were very short (12 milliseconds average at -40° F) and increased with increase in concentration of either triethylamine or n-heptane; the delays were shorter with triethylamine. Several ethylenimine blends gave the following average ignition delays:

Blending agent (percent by volume)	Average ignition delay (milliseconds)	
	-40° F	-105° F
50-n-Heptane	60	104
70-n-Heptane	243	No ignition
50-Triethylamine	14	33
70-Triethylamine	24	178

4. Substitution of a 2-alkyl group appreciably reduced the self-igniting property of ethylenimine.

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[redacted]

TABLE I - LOW-TEMPERATURE IGNITION DELAYS OF ALLYLAMINE, DIALLYLAMINE, AND THEIR TRIETHYLAMINE BLENDS WITH LOW-FREEZING RED FUMING NITRIC ACID

[Acid supercooled at -105° F]

Fuel (percent by volume)	Temperature (°F)	Number of trials	Ignition delay (milliseconds)			Remarks
			Minimum	Maximum	Average	
100-Allylamine	-40	3	80	98	91	
	-76	4	108	131	122	Data from timer
	-105	4	90	237	155	
50-Allylamine-50-Triethylamine	-40	4	19	22	21	
	-76	6	18	42	27	
	-105	5	32	67	50	
30-Allylamine-70-Triethylamine	-40	6	16	29	22	
	-76	4	29	52	41	
	-105	5	148	857	360	
15-Allylamine-85-Triethylamine	-40	4	28	55	39	
	-76	4	238	913	507	
	-105	2	---	---	---	No ignition
100-Triethylamine	-40	4	266	647	422	
	-76	4	---	---	---	No ignition
	-105	2	---	---	---	No ignition
100-Diallylamine	-40	3	35	63	47	
50-Diallylamine-50-Triethylamine	-40	6	23	301	87	
30-Diallylamine-70-Triethylamine	-40	4	53	515	210	

TABLE II - LOW-TEMPERATURE IGNITION DELAYS OF MIXED ALKYL THIOPHOSPHITES AND MIXED ALKYL THIOPHOSPHITES-TRIETHYLAMINE BLENDS WITH LOW-FREEZING RED FUMING NITRIC ACID

[Acid supercooled at -105° F]

Fuel (percent by volume)	Temperature (°F)	Number of trials	Ignition delay (milliseconds)			Remarks
			Minimum	Maximum	Average	
100-Mixed alkyl thiophosphites	-40	6	5	17	9	
	-76	2	8	9	9	Explosions
	-105	4	1022	1503	1265	
50-Mixed alkyl thiophosphites - 50-Triethylamine	-40	4	11	19	15	
	-76	4	20	32	24	
	-105	2	----	----	----	No ignition
30-Mixed Alkyl thiophosphites- 70-Triethylamine	-40	4	23	35	29	
	-76	4	29	52	41	
	-105	2	----	----	----	No ignition

TABLE III - LOW-TEMPERATURE IGNITION DELAYS OF ETHYLENIMINE FUELS AND THEIR TRIETHYLAMINE AND n-HEPTANE BLENDS WITH LOW-FREEZING RED FUMING NITRIC ACID

[Acid supercooled at -105° F]

Fuel (percent by volume)	Temperature (°F)	Number of trials	Ignition delay (milliseconds)			Remarks
			Minimum	Maximum	Average	
100-Ethylenimine	-40	2	11	13	12	Explosions
	-105	1	---	---	---	Explosion
50-Ethylenimine - 50-Triethylamine	-40	4	11	17	14	Data from timer
	-105	6	27	51	33	Data from timer
30-Ethylenimine - 70-Triethylamine	-40	3	16	32	24	Data from timer
	-105	4	29	335	178	Data from timer
15-Ethylenimine - 85-Triethylamine	-40	4	53	189	106	Data from timer
	-105	2	---	---	---	No ignition
50-Ethylenimine - 50-n-Heptane	-40	3	15	95	60	Data from timer
	-105	4	54	219	104	Data from timer
30-Ethylenimine - 70-n-Heptane	-40	4	186	290	243	Data from timer
	-105	2	---	---	---	No ignition
15-Ethylenimine - 85-n-Heptane	-40	2	---	---	---	No ignition
	-105	2	---	---	---	No ignition
100-2-Ethylethylenimine	-40	5	26	55	39	

TABLE IV - COMPARISON OF AVERAGE IGNITION DELAYS OF ALLYLAMINE, MIXED ALKYL THIOPHOSPHITES, ETHYLENIMINE, AND THEIR TRIETHYLAMINE BLENDS WITH LOW-FREEZING RED FUMING NITRIC ACID

Blend (percent by volume)		Average ignition delay (milliseconds)		
Fuel	Triethylamine	Allylamine	Mixed Alkyl thiophosphites	Ethylenimine
Temperature, -40° F				
100	0	91	9	[a]12
50	50	21	15	14
30	70	22	29	24
15	85	39	---	106
0	100	422		
Temperature, -76° F				
100	0	122	9	---
50	50	27	24	---
30	70	41	41	---
15	85	507	---	---
0	100	(b)		
Temperature, -105° F (acid supercooled)				
100	0	155	1265	(a)
50	50	50	(b)	33
30	70	360	(b)	178
15	85	(b)	---	(b)
0	100	(b)		

[a]Explosions.
[b]No ignition.

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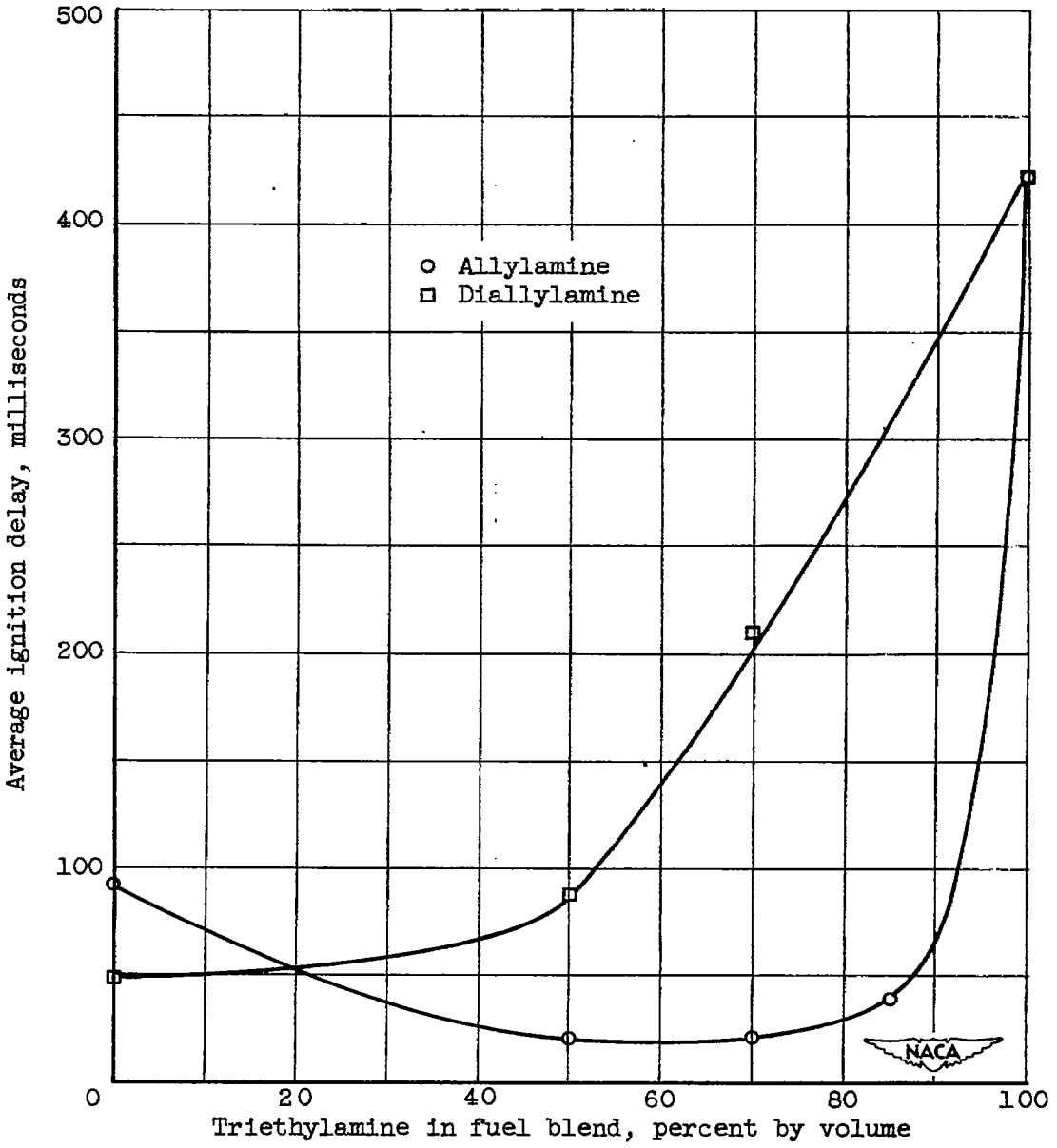

Figure 1. - Average ignition delays of allylamine, diallylamine, and their triethylamine blends at -40° F. Oxidant, low-freezing red fuming nitric acid.

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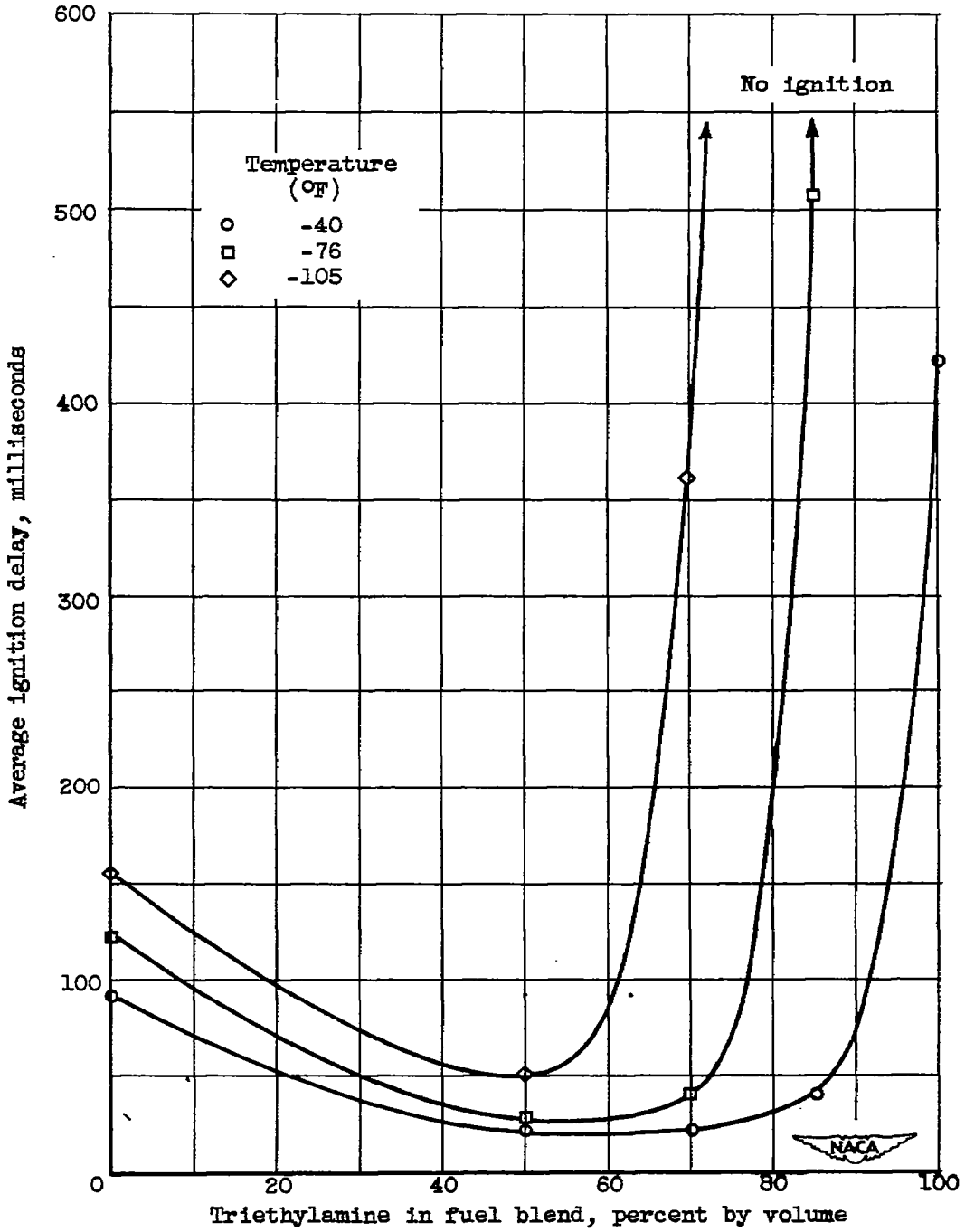

Figure 2. - Average ignition delays of allylamine and its triethylamine blends at -40°, -76°, and -105° F. Oxidant, low-freezing red fuming nitric acid. (Acid supercooled at -105° F.)

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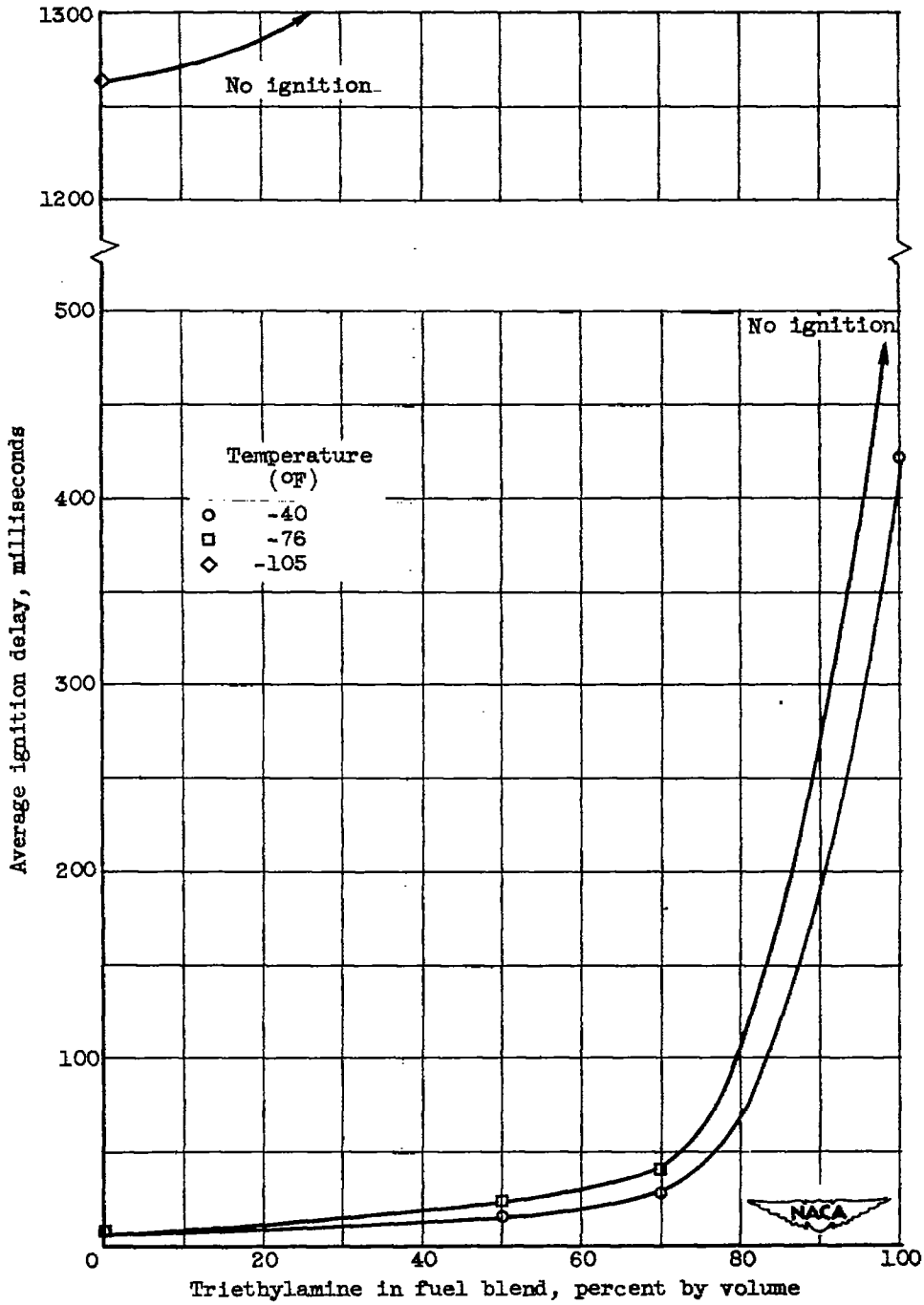

Figure 3. - Average ignition delays of mixed alkyl thiophosphites and its blends with triethylamine at -40°, -76°, and -105° F. Oxidant, low-freezing red fuming nitric acid. (Acid supercooled at -105° F.)

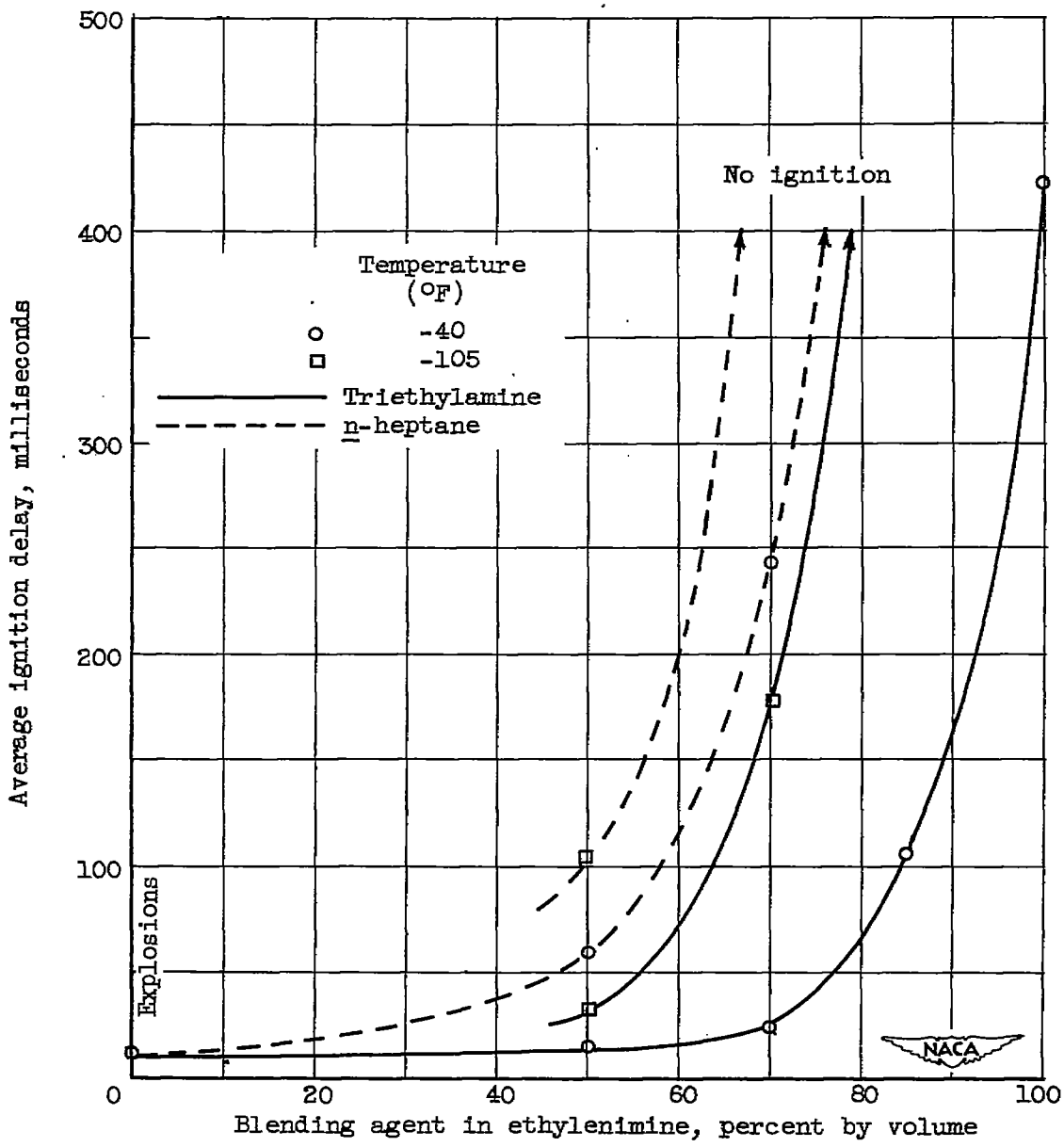

Figure 4. - Average ignition delays of ethylenimine and its triethylamine and n-heptane blends at -40° and -105° F. Oxidant, low-freezing red fuming nitric acid. (Acid supercooled at -105° F.)

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